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Relation of Raman Effect to Crystal Structure and Properties of Diamond.

By

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(Plate IX.)

Abstract.

The results of a study of the Raman effect and certain attendant phenomena in nine different samples of diamond are described. All of them show Raman lines corresponding to one well defined frequency shift $1331{\cdot}9 \pm 0{\cdot}3$, the value of which does not show any detectable variation from diamond to diamond. In perfect and colourless samples, the Raman lines are usually very intense and sharp, whereas in blue diamonds there appears to be a weakening of the absolute intensity. In one rather poor sample the line presents a distorted appearance. There is present in all cases, except one very yellow sample, a system of three bands at 4131, 4157 and 4174 A.U., the central one being very prominent and extending over 10 A.U. A prominent continuous spectrum often accompanies the above having a well defined limit on the violet side at about 4240 A.U. and extending well into the red end. The intensity of these bands and the continuous spectrum varies in a remarkable way with the specimen studied; they are weak in white diamonds and are particularly conspicuous in blue diamonds for the colour of which they appear to be responsible.

Considering each carbon atom as bound tetrahedrally to its four nearest neighbours and together with them capable of oscillation with respect to the rest of the crystal lattice, a theoretical computation indicates

four fundamental oscillations whose wave-numbers are 440, 780, 1306 and 1750. The third gives approximately the frequency-shift of the observed Raman lines and represents an oscillation of the central carbon atom within the tetrahedron. The higher frequencies observed by Robertson and Fox in the infra-red absorption are explained as combinations of the above. Existing data on the specific heat of diamond and other physical properties are briefly discussed in relation to the above frequencies.

1. *Introduction.*

In a recent paper[1] the author gave some measurements of the frequency shifts observed in the Raman effect with diamond. Certain attendant phenomena which were observed suggested that a more detailed study with as many different samples of diamond as possible would be of interest. The present paper describes the experimental results obtained with nine diamonds of different colours, sizes and degrees of perfection. The relation between the observed phenomena and the crystal structure and other properties of diamond are discussed in detail.

2. *Experimental results.*

The light of a quartz mercury arc is focussed by means of a glass condenser on to the diamond which is so mounted that the reflected light is sent in a direction opposite to that of the spectrograph. A two prism glass instrument of high light gathering power supplied by Adam Hilger is used for photographing the spectra of the scattered light.

In the first instance it must be mentioned that with all the diamonds, Raman lines were observed corresponding to one well defined frequency shift of about 1332 wave-numbers, whose value does not show any detectable variation from diamond to diamond. Using Hartman's simplified formula

[1] Ind. Jour. Phys., Vol. V, p. 35 (1930). See also Ramaswamy, Nature, Vol. 125, p. 704 (1930) and Ind. Jour. Phys., Vol. V, p. 96 (1930). The effect was described by him first in these communications.

with the mercury lines as standard the following frequency shifts are obtained in a variety of them; five different samples of colourless diamond: 1331, 1332, 1332, 1331 and 1331; yellow diamond: 1330; blue diamond: 1333, 1331. It will be seen that the variations are within the limit of the accuracy of the method. In most cases the transition is excited by the two principal mercury lines 4046 and 4358 A.U., the line arising from the latter being usually the stronger. Three plates have also been measured interpolating linearly between close iron arc lines. The frequency shifts obtained are 1331·7, 1331·9, and 1332·1. Thus the best representative value for the infra-red wave-number may be given as $1331{\cdot}9 \pm 0{\cdot}3$.

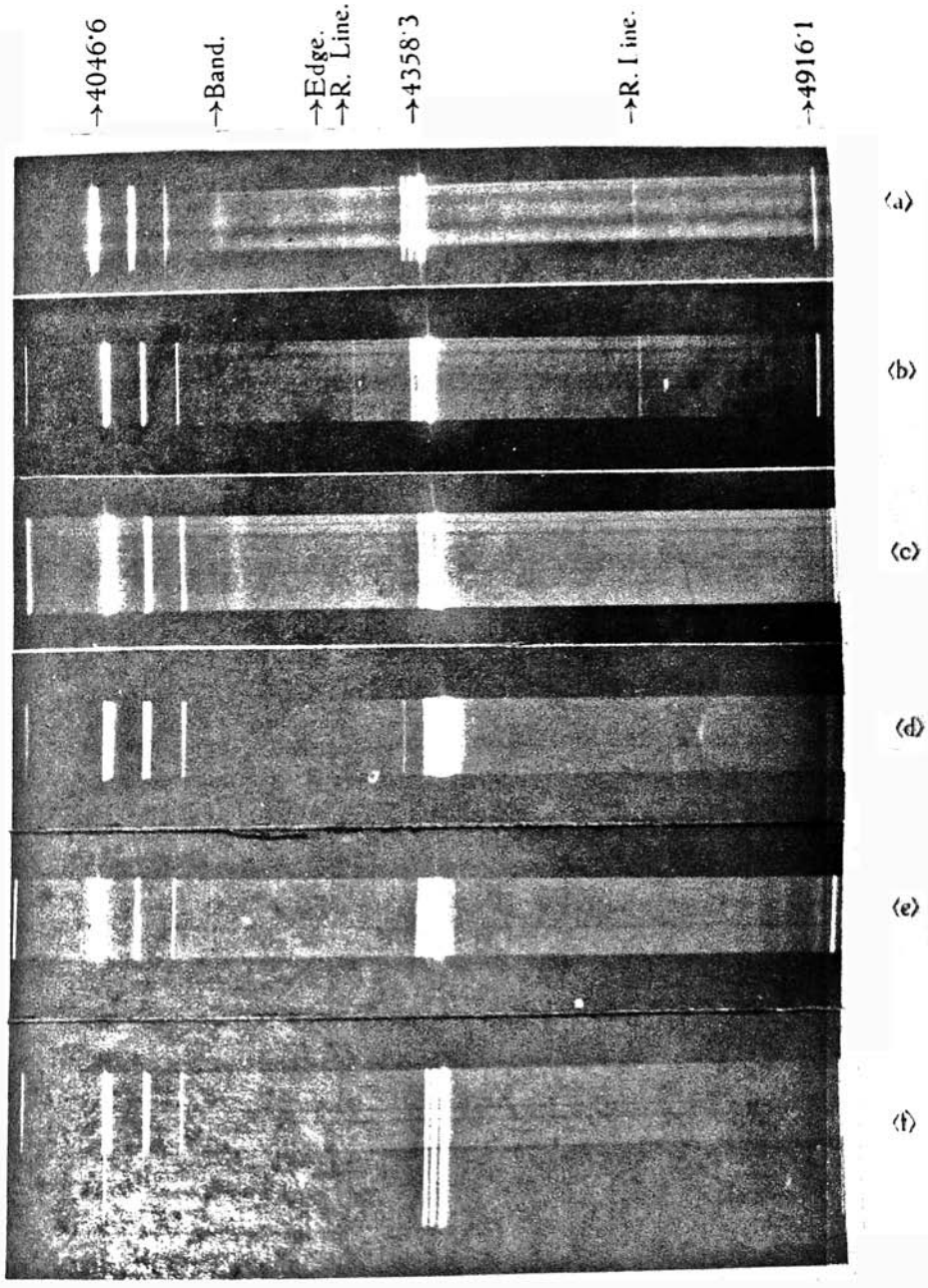
An important feature associated with this line is the extreme sharpness in most cases. Hence the corresponding wave-number may be regarded as a physical constant characteristic of diamond capable of being measured with a high degree of precision. Such an extreme sharpness, according to the views expressed by Sir C. V. Raman, may be connected with the perfection of crystal structure in diamond. In one case however, when the diamond was of a rather poor quality it was found that the sharpness of the line is considerably diminished, the line presenting a slightly distorted appearance. There is also present a feeble companion line on its longer wave-length side and but so diffuse that its genuineness is uncertain.

It is found that under suitable conditions of illumination, this principal Raman line could be photographed with ease in about 5 to 10 minutes in the case of diamonds of moderate size whereas an hour's exposure is usually quite sufficient in the case of even the smallest of those examined. Contrary to this there is however present a certain amount of difficulty in obtaining this line with diamonds of a light blue colour, although it must be mentioned here that there is a much stronger continuous spectrum in the latter case. It will no doubt have to be remembered that the intensity of the

scattering depends to a large extent on the particular cut, adjustment and various other factors associated with the examination of each sample. On a close examination of the various plates taken with colourless and with blue diamonds, the author is definitely led to conclude that the greater prominence of the continuous spectrum with the latter cannot alone account for the difficulty of obtaining the Raman lines. It appears that there is a real weakening of the intensity of the Raman lines, along with the development of the continuous spectrum in blue diamonds. See Figs (c) and (f) in Plate IX.

Bands and the continuous spectrum.—Besides the Raman lines there is present a system of three bands at wave-lengths 4131, 4157 and 4174 A.U. The central one is the most intense one and is comprised between well defined limits extending over 10 A.U. *viz.*, from 4152 to 4162. The other two bands are relatively much feebler. It must be mentioned here that on the longer wave-length of the mercury line 4358, there is nothing corresponding to any one of these bands. This result clearly shows that the band does not represent a Raman transition. If it was excited in the manner of a Raman line by the 4046 radiation, it is but natural to expect the 4358 to produce it quite as prominently if not stronger. The light scattered by one of the samples was also photographed with a quartz spectrograph. The spectrum shows the Raman lines excited by the group of lines at 3650 A.U. quite prominently whereas there is nothing excited by this group corresponding to the above bands of the blue violet region. The plate is also free from continuous spectrum in this region. Walter[1] has actually observed bands at 4155 in the absorption spectrum of some diamonds. The effect was marked in some yellow ones, but feeble in red, green and brown diamonds. The fact that there does exist such an absorption frequency

[1] Wied. Ann., Vol. 42, p. 505 (1891).



Raman Spectra of Diamonds.

(a) Light Yellow; (b) Colourless; (c) Blue; (d) Imperfect; (e) Yellow; (f) Blue.

in diamonds suggests that they are in the nature of fluorescent radiation.

The intensity of these bands varies in a remarkable manner with the colour of the diamond, (Plate IX). Those having a pale blue colour show the phenomenon most conspicuously (Fig. c), whereas they are much less prominent in colourless diamonds (Fig. b). (Fig. e) was obtained with a diamond of a strikingly yellow colour. It gave feeble Raman lines and a continuous spectrum (without bands) stretching practically over the whole region from 3800 A.U. to the red end. Crookes[1] has recorded various sharp lines in the green and the greenish blue region of the phosphorescent spectrum of diamond excited by exposure to cathode rays. In his work, there is no mention of any bands analogous to those mentioned in this paper. This result is surprising as one would expect them to be excited quite as prominently.

Another striking feature characterising the scattered spectra is the presence of a strong continuous spectrum which appears with a fairly well defined edge on the violet side at about 4240 A.U. and extending well into the red end of the visible spectrum. All the plates taken with various diamonds show a gap between the mercury lines 4916 and 5460. A visual examination through the spectroscope reveals that the continuous spectrum is quite as prominent in this region as in others. The above result is therefore due to the fact that the photographic plate is insensitive in this region. In some cases there is also present a feeble continuous spectrum in the region 3800 to 4100 A.U. The introduction of a filter cutting out the mercury line at 4046 eliminates the bands and practically the whole of the continuous spectrum (Fig. f). Figs. a, b, c and e serve to show very clearly the variation of the above phenomenon in diamonds. Fig. a is a spectrum taken with a diamond having the palest yellow

[1] Phil. Trans., Vol. 170, pp. 135 and 641 (1879). See also Vol. 174, p. 891 (1883).

tinge and shows both the Raman lines and the bands accompanied by a continuous spectrum of considerable intensity.

The continuous spectrum in blue diamonds is so conspicuous (Fig. c) that the aggregate intensity of the same must be very considerable and is probably responsible for its blue colour. One of the samples examined which was ordinarily (in dull light) was of a light blue colour showed a remarkable strengthening of the blue when taken into the bright day light. This sample was illuminated with the near ultra-violet light from a mercury arc lamp by interposing a Wood's ultra-violet filter and was found to emit a marked blue radiation. Becquerel[1] observed in the phosphorescent spectrum of diamond two bands from 4300 to 4860 and 5270 to 6560 A.U. which are probably closely related to the above phenomena.

3. *Relation to Crystal Structure.*

The structure of the diamond lattice has been very thoroughly determined by Bragg and others and is now regarded as a continuous chain of carbon atoms linked to each other in such a manner that every carbon atom is joined to four others tetrahedrally. The lattice is made up of two interpenetrating face-centred cubic lattices. It is reasonable to assume that the observed Raman transition represents an oscillation of individual carbon atoms within the core constituted by the rest of the lattice surrounding each one of them. Such a view is strongly supported from the consideration of the following cases. The author has recently investigated the Raman spectra of various tetra-chlorides having tetrahedral structures.[2] All of them show four frequencies, the third of which is the most prominent. In the series, as we proceed from carbon the lightest to tin the

[1] Ann. Chim. Phys., Vol. 55, p. 89 (1759).
[2] *Loc. cit.*

heaviest, this intense line appears to gain in prominence at the expense of others. The cases of SO_4 and ClO_4 have again analogous tetrahedral structures and likewise show one prominent line accompanied by a few other feeble lines.[1] From a consideration of the mechanical vibrations of such a system, the author has identified this line with an oscillation in which the central atom moves about its equilibrium position within the surrounding tetrahedron.[2] All the above cases result in an intense and well polarised Raman line, very much like that of diamond.[3]

It must however be remembered that in the case of diamond we are not justified in isolating portions of the lattice in as much as it is one big molecule extending to the very boundaries of the crystal. It is but natural to assume that the character of the line will be influenced to some extent by the dimension of the outer core surrounding the oscillating atom. In this connection the theory of mosaic structure developed by Smekal, Zwicky and others is of interest in that it postulates an intrinsic imperfection of crystals. A typical instance of such a mosaic structure showing itself in diamond is actually known and may be cited here. The reflection of Rh—Kα doublet comes out with extreme sharpness from an ideal diamond whereas it shows a large distortion and breadth in an imperfect one.[4] Similar variations in the sharpness of the Raman lines have actually been observed and reported in the previous pages. Such phenomena are evidently connected with the degree of imperfection or mosaic state. Whether the intensity of the Raman line, particularly in blue diamonds, is also influenced by such imperfections is more than can be said just now. To ascertain the precise relation between the mosaic

[1] A. M. Taylor, Mol. Spectra and Mol. Structure, Trans. Far. Soc., p. 830 (1929).

[2] Ind. Jour. Phys., Vol. 5, p. 73 (1930).

[3] Ramaswamy (*loc. cit.*) finds that the line in diamond is well polarised.

[4] Handbuch, Der Ang. Phys. Chem., Band 14, p. 436 (1926).

state and the Raman scattering, it is however necessary to examine the same diamond more critically by various methods.

4. *Relation to Infra-red Absorption.*

Each atom of the diamond lattice may be considered as being influenced by only the four nearest neighbours arranged tetrahedrally, the latter in their turn being bound similarly to others which may be regarded as being rigidly fixed. The mechanical vibrations of such a configuration can be worked out in a manner very similar to that of the AX_4 type. The potential energy function in this case undergoes a slight change in view of the fact that the X atoms are also bound tetrahedrally. If the constant[1] which represents the force between neighbouring carbon atoms in the diamond lattice is taken as $43{\cdot}35 \times 10^4$, it can be shown that the frequencies with which the system is capable of oscillating are given by 440, 780, 1306 and 1750. The analysis shows that 780 and 1750 correspond to a symmetric motion of the outer carbon atoms, whereas 1306 is analogous to the intense oscillation in the tetrahedral models. It can at once be identified with the actually observed one at 1332 and represents an isotropic vibration of the carbon atom within the surrounding core. It is also obvious, by analogy with other cases, that the rest of the postulated frequencies, *viz.*, 440, 780 and 1750 will manifest themselves very weakly in the Raman spectra, if they do so at all. On the other hand, it is quite possible that when the entire lattice is taken into consideration, these frequencies may undergo considerable alterations and thus are more or less virtual.

[1] The justification for such a value of the constant is that it gives 990 for the C—C oscillation frequency of ethane in perfect agreement with the experimental value.

The case of methane investigated by Dennison[1] is instructive in this connection. Its Raman spectrum[2] has so far revealed only one prominent multiple band at about $3{\cdot}5\mu$ which is analogous to the principal line in all the above cases and is identified by Dennison with such an oscillation. The other three frequencies demanded by the theory have not however so far been detected at all.

Of the above four calculated frequencies, the one at 1306 corresponds to an optically active oscillation and is represented by one edge of a broad band at $8{\cdot}02\ \mu$ in the infra-red absorption.[3] Why such a sharp line in the Raman spectra should have in the infra-red absorption, a broad band with its centre displaced to one side as its analogue is not clear. This result is of great significance in that it affords a definite case where the infra-red absorption is of quite a different character from that of the Raman line. Of the other three oscillations, those having values 780 and 1750 are optically inactive and accordingly have not been observed by Robertson and Fox in the absorption spectrum.[4] The one at 440 is beyond the region of their investigation.

On the other hand they have detected three more bands at 2086, 2438 and 3353, the last of which has been interpreted by them as having a combinational origin. The former two are regarded as fundamental oscillations characteristic of the diamond lattice. The author is however of the opinion that they all have a combinational origin as the former two may also be represented satisfactorily as summationals of the frequencies postulated above. The table below shows their mutual relationship.

1 Astrophys. Jour., Vol. 62, p. 84 (1925).

2 J.C. Mclennan, H. D. Smith and J.O. Wilhelm, Trans. Roy Soc. Canada, Vol. 23, p. 279 (1929).

3 Robertson and Fox, Nature, Vol. 125, p. 704 (1930).

4 Analogous oscillations in methane at 1520 and 4200 appear very feebly in the infra-red absorption. D. M. Dennison, *loc. cit.*

Fundamentals	Raman effect	Infra-red R. and F.	Interpretation
ν_1 : 440	...	...	...
ν_2 : 780	...	Inactive	...
ν_3 : 1306	1332	1246	ν_3
ν_4 : 1750	...	Inactive	...
...	...	2086	2086 : $\nu_2 + \nu_3$
...	...	2438	2526 : $\nu_1 + \nu_2 + \nu_3$
...	...	3353	3392 : $\nu_2 + 2\nu_3$

The agreement is good in view of the fact that the method is only approximate. It must be mentioned that the above theory is only tentatively put forward.

5. *Relation to Specific Heat.*

The case of diamond is of great interest as it is the classical example of a solid element which does not conform to the Dulong and Petit law of atomic heats. The measurements of Nernst[1] show that the specific heat falls to almost nothing at low temperatures and is not even a thousandth part of what is to be expected on the basis of the above law. The theory developed by Debye for the specific heat of solids enables us to connect the natural frequencies of a lattice with the observed specific heat and its variations with temperature. Θ, the characteristic temperature of the substance is connected with ν_m the maximum oscillation frequency of the lattice by the equation $\Theta = \frac{h\nu_m}{k}$ where h is the Planck's quantum of action and K the molecular gas constant. From the specific heat measurements at moderately high temperatures, the value of this constant is given by Nernst and Lindemann[2] as 1860

[1] Ann. Der. Phys., Vol. 36, p. 395 (1911).
[2] See Handbuch Der. Physik, Vol. 10, p. 42.

which corresponds to a wave-number of about 1300. This is in fair agreement with the observed principal frequency.

On the other hand such a low value of the characteristic temperature is not in agreement with the observations at low temperatures. The failure of the theory is evidently due to the fact that it assumes a maximum limit for the possible frequencies. The characteristic temperature assumed above, *viz.*, 1860 does not really correspond to the highest of the frequencies for diamond, *viz.*, 1750 according to the calculations given in the previous pages. Simon [1] discussed more fully the available data and was led to explain the observed specific heat variations of diamond as due to a resultant effect of two different functions only one of which is of the Debye type. It is interesting to note here that the characteristic temperature appearing in it, *viz.*, 2340 closely corresponds to the highest of the calculated frequencies, *viz.*, 1750. It may be hoped that a careful consideration of the various theories and further experimentation will lead to a satisfactory explanation of the interesting observations connected with the specific heat of diamond.

6. *Relation to other Physical Properties.*

It is well known that the Debye function of a substance can also be deduced from a knowledge of the Poisson's ratio and compressibility. The results obtained in various cases are in good agreement with the values deduced from specific heat data.[2] In the case of diamond the data for the Poisson's ratio are however not available. On the other hand Grüniesen [3] has given a theory connecting this function with the co-efficient of volume expansion. In the case of diamond it

[1] Sitz-der Preuss. Akad. der Wiss., Vol. 33, p. 477 (1936).
[2] See Born. 'Dynamik der Kristalgitter.'
[3] Handbuch der phys., Vol. 10, (loc. cit.)

has been worked out by him as 1860 almost in perfect agreement with the value of Nernst and Lindemann at higher temperatures. This again suggests a frequency of 1300 for the lattice.

Apart from its relation to the above physical constants, it may be expected that such a high frequency of the nuclear oscillations also involves a correspondingly high electronic frequency lying in the far ultra-violet responsible for its large optical refractivity and dispersion. An actual computation on the basis of Haber's square-root formula[1] yields an absorption wave-length of about 500 A. U. for diamond. Such an absorption is too far in the ultra-violet and will not account satisfactorily for the observed refractivity and dispersion of diamond. It will however have to be remembered that Haber's rule involves various assumptions. The significance of the same has been discussed very thoroughly by Born.[2] The rest-strahlen frequency in cases like rock salt, sylvine, etc., could be satisfactorily connected with their ultra-violet absorption. It is interesting to note that the rule apparently fails in the case of diamond, which may be due to the fact that unlike the former cases of ionic lattices, diamond has a lattice built out of homopolar bonds.

7. *Relation to the Colour.*

It is suggested that the aggregate intensity of the bands and the continuous spectrum is responsible for the blue colour of diamonds. The attribution of this blue colour to the emission of such secondary radiations is not exceptional to diamond. A strikingly analogous case is that of crystalline anthracene which often exhibits a bluish-green tint due to fluorescence. Such a view for the origin of

[1] Verh d. D. Phys. Gps., Vol. 13, p. 1117 (1911).
[2] Born, *loc. cit.*

the blue in diamonds is very significant especially if it is recalled that the author has been able to photograph these bands as well as the continuous spectrum throughout the entire region even in reasonably clear and colourless diamonds, although their intensity is much less in comparison with the blue ones. This weakening in intensity of these secondary radiations with increasing clearness of the diamond, leaves it uncertain whether in the limiting ideal case of a colourless diamond the phenomenon would altogether disappear. For some reason it develops and attains a degree of prominence in particular samples resulting in a blue colour of sufficient intensity as to affect the eye ordinarily. The precise significance of the absorption frequencies of diamond in terms of its electronic structure is however not clear. The case of coloured rock salt is of interest in this connection as it is now known that the colour is not due to any contamination. Even the samples which are chemically pure show the phenomenon. In this case it is attributed to absorption of light by free neutral sodium atoms present in the lattice.

Finally, mention may be made here of an interesting property of diamond, *viz.*, its photoconductivity investigated in detail by Gudden and Pohl.[1] Their results show that every absorbed quantum of energy $h\nu$ liberates one electron. Such electrons are transferred to small distances by an external electric field and are responsible for the photoconductivity. Such an electronic disturbance must in some manner be related to the various other optical phenomena mentioned in this paper such as absorption, fluorescence, phosphorescence, Raman effect and colour. That Raman effect has also been classed amongst these need not be surprising if we recall here the views originally expressed by Sir C. V. Raman. The mechanism of the phenomenon as pictured by him essentially involves the electron, in that the incident light quantum tends

[1] Zeit. f. Phys., Vol. 17, p. 331 (1923).

initially to disturb the electron but its insufficient energy renders the attempt unsuccessful and results in a nuclear disturbance. Whether there is any real mutual relationship between the above phenomena and if so its precise nature, or if they are entirely independent and co-existing can only be decided with certainty after further experimentation.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for suggesting the problem and giving many helpful suggestions in the course of the work. Grateful acknowledgments are also due to Sir Onkarmal Jatia, Mr. Nirmal Chunder Chunder, Mr. R. Ramjeedass Iyer, Messrs. Thakorlal Hiralal and Messrs. the Oriental Gem and Jewellery Co., whose kindness in loaning valuable diamonds made this investigation possible.